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(54) Molybdenum material for structural material purposes

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(72) Inventor: M. Kiyomiya
c/o Tokyo Shibaura Denki K.K., Yokohama Kinzoku Kojo, 8 Shinsugitacho, Isogo-ku, Yokohama-shi, Japan

(72) Inventor: T. Shimizu
c/o Tokyo Shibaura Denki K.K., Yokohama Kinzoku Kojo, 8 Shinsugitacho, Isogo-ku, Yokohama-shi, Japan

(71) Applicant: K.K. Toshiba
72 Horikawacho, Saiwai-ku, Kawasaki-shi, Japan

(74) Agent: Patent Attorney S. Tsukuni

SPECIFICATION

1. Title of the Invention

Molybdenum for structural material purposes

2. Scope of the Patent Claims

1. Molybdenum for structural material purposes, characterized in that from 1 to 5 wt% of lanthanum oxide (La_2O_3) is dispersed uniformly in molybdenum (Mo), and the average particle size of said dispersed lanthanum oxide (La_2O_3) is not more than 3 μm and the maximum particle size is not more than 7 μm.

2. Molybdenum for structural material purposes, according to Claim 1, where a sinter comprising molybdenum (Mo) powder and lanthanum oxide (La_2O_3) powder has been subjected to working with a working factor of at least 60%.

3. Detailed Description of the Invention

Technical Field of the Invention

The invention concerns molybdenum for structural material purposes where La_2O_3 particles are uniformly dispersed in Mo.

Prior Art of the Invention and Associated Problems

Mo material in which La_2O_3 is included is supplied mainly as a coil-like (spiral-like) wire or as a plate formed into a round cone as a cathode material for electron tubes.

The La_2O_3 in the Mo does not form a solid solution and a compound with the Mo in the same way as the ThO_2 in thorium oxide-containing tungsten (ThO_2-W) and it is dispersed as La_2O_3 particles in the Mo.

Consequently, the various characteristics of such molybdenum materials are greatly affected not only by the La_2O_3 particle content but also by the state of dispersion of the particles. For example, in cases where the La_2O_3 in the Mo aggregates and the state of dispersion of the La_2O_3 particles is poor problems arise in that failure often occurs, or cracks are formed, on

secondary working of the material such as when forming a coil or a cone for example.

Furthermore, if the state of dispersion of the La_2O_3 in the Mo is poor, as mentioned above, then various problems arise when the material is used as the cathode material for an electron tube in that it is difficult to achieve good electron release characteristics and the life expectancy is short.
Hence, in the past it has been impossible to resolve the various problems associated with workability and electron release characteristics, for example, as mentioned above since the appropriate dispersion state of the La_2O_3 added to the molybdenum material was unknown.

Purpose of the Invention

The aim of the present invention is to resolve the abovementioned problems by supplying Mo material which contains from 1 to 5 wt% of La_2O_3 which, when used as a structural material, can be subjected easily to secondary working and which, when used as a cathode material, has a long life.

Outline of the Invention

As a result of thorough research carried out with a view to achieving the abovementioned aim, the inventors have discovered that if, in a Mo material which contains from 1 to 5 wt% of La_2O_3, the La_2O_3 particles are uniformly and finely dispersed, the various properties such as the secondary working properties and the electron release characteristics are improved, and the invention is based upon this discovery.

The molybdenum for structural purposes of this invention is characterized in that from 1 to 5 wt% lanthanum oxide (La_2O_3) is uniformly dispersed in molybdenum (Mo) and the average particle size of said dispersed lanthanum oxide (La_2O_3) particles is not more than 3 μm and the maximum particle size is not more than 7 μm.

In this invention the La_2O_3 is a component which provides an electron release function and increases the high temperature strength.

The La_2O_3 content is set at from 1 to 5 wt%. If the La_2O_3 content is less than 1 wt% then the effect of adding La_2O_3 is unlikely to be achieved and characteristics approaching those of pure Mo are exhibited, and if the content exceeds 5 wt% then little change over the effect observed on adding not more than 5 wt% is seen and, moreover, there are problems in that, for example, the secondary working properties become poor.

The particle size of the La_2O_3 must be not more then 3 µm as an average particle size and not more than 7 µm as a maximum particle size. If the average particle size exceeds 3 µm or if the maximum particle size exceeds 7 µm then not only are the working properties adversely affected in that failure may occur or cracks may be formed on secondary working a wire or sheet, but when the material is used as the cathode material in an electron tube it is difficult to achieve stable electron release characteristics over a long period of time.

Moreover, the secondary working properties of a wire or sheet material are affected by the working factor (fractional change in the cross sectional area) from a sinter comprising molybdenum (Mo) and lanthanum oxide (La_2O_3) as well as the content and state of dispersion of the La_2O_3.

Molybdenum for structural purposes of this invention is preferably worked with a working factor from the sinter of at least 60%. Metals like Mo which, when compared with Cu and Al, are brittle, are such that the non-orientated crystal structure produced by sintering can be formed into a crystal structure which is orientated in the working direction by working. The flexibility of the molybdenum for structural purposes is improved by forming such an aggregate structure. According to the results of experiments carried out by the inventors, with Mo material which contains from 1 to 5 wt% La_2O_3, secondary working becomes easier as the working factor from the sinter

becomes great, and there is no problem in practice with wire or sheet material where the working factor is at least 60%.

Embodiment of the Invention

The characteristics of Mo materials containing from 1 to 5 wt% of La_2O_3 of this invention are described below.

Pressed-powder mouldings were made with a pressure of 1.5 ton/cm^2 using a mechanical press in accordance with the methods of powder metallurgy while varying the amount of La_2O_3 added and the method of mixing in such a way that the La_2O_3 content was 0.5, 1.0, 2.0, 4.0 or 6.0 wt% and the particle size of the La_2O_3 differed, and the pressed-powder mouldings were sintered for 8 hours at 1850°C in a hydrogen atmosphere. The sinters obtained at this time were of specific gravity about 9.50, and there were of a form of cross section 12 x 12 mm and length 650 mm. The sinters were subjected to beating and drawing while applying heat and wires of 0.60 mmϕ were obtained. Verification of the La_2O_3 particle size in the Mo wires was carried out by embedding the wire in a thermoset resin and providing a mirror surface finish with the usual polishing method and then just the Mo material was polished away using a special electrolytic polishing method so that the La_2O_3 was left behind above the polished surface and then the particles were observed using a scanning electron microscope.

The relationships between the La_2O_3 content in the Mo in the 0.60 mmϕ diameter wires and the maximum La_2O_3 particle size with the flexibility of the wire and secondary recrystallization temperature are shown in Table 1.

Table 1

La_2O_3 Content (%)		0.5			1.0			2.0				4.0			8.0	
Maximum La_2O_3 Particle Size (µm)		1.2	5.3	9.2	1.1	4.9	9.6	0.9	4.5	8.0	9.7	0.9	5.2	9.4	0.9	4.5
Number of Flexes of the 0.6 mmϕ (Relative Comparison)	Drawn Worked	14	8.0	1.3	10.1	8.0	0.9	9.6	8.0	0.9	0.4	9.0	7.9	0.5	1.3	0.1
	After 3 min at 1500°C Anneal	10	8.0	1.2	4.0	3.8	0.7	4.5	4.0	0.3	0.3	4.0	3.5	0.6	7	0.1
Secondary Recrystallization Temperature of 0.6 mmϕ (°C)		1400	1400	1400	1700	1700	1700	1800	1800	1800	1750	1750	1750	1750	1750	175

As is clear from these results, an La_2O_3 content of from 1.0 to 5 wt% is best, and according to the experimental results obtained by the inventors an La_2O_3 content of from 2 to 3 wt% is ideal. Furthermore, a smaller La_2O_3 particle size is better, and the secondary working properties decline sharply if the particle size exceeds 8 μm.

Furthermore, the abovementioned pressed-powder mouldings were pressed at a hydrostatic pressure of 2 ton/cm² to mould pressed powder-mouldings and sinters of specific gravity 9.45 and with a shape of diameter 60 mmϕ and length 400 mm obtained by sintering for 8 hours at 1850°C in a hydrogen atmosphere were hammer worked and roll worked and sheets of thickness 0.2 mm were obtained. At this time an intermediate heat treatment above the secondary recrystallization temperature was carried out in a hydrogen atmosphere. The dimensions of the sheet material which was heat-treated were such that the working factor to work to a sheet thickness of 0.2 mm was 40%, 60% or 80%. The results obtained on investigating the flexibility of the sheet materials at this time are shown in Table 2.

Table 2

Working Factor (%)	40	60	80
Flex Properties of 0.2 t sheet material (Relative Values)	1.5	10	20

* Amount of La_2O_3 added: 2%
Maximum particle size of the La_2O_3: 2.0 μm

As is clear from these results, the effect on the flexibility of the working factor is similar to that in the case of a wire where it is known that good flexibility is obtained on working by at least 60%

Next, the relationship between the La_2O_3 content in the Mo used in an electron tube (wire diameter 0.2 mmϕ) and the electron release characteristics is shown in Table 3. According to Table 3 an La_2O_3 content of at least 1.0 wt% is required, and there is no improvement in the electron release characteristics even if the La_2O_3 content exceeds 6.0 wt%, there being a slight

fall when compared with the characteristics obtained with 2 wt%.

Table 3

La_2O_3 Content (%)	0.5	1.0	2.0	6.0
Initial Electron Release Characteristics (Cathode heating temperature 1600°C) (Relative value)	1	15	25	14
Life (Relative value of the time period over which stable continuous electron discharge characteristics are obtained)	1	13	18	13

Effect of the Invention

As is clear from the description above, the molybdenum for structural purposes of this invention provides the following excellent effects: (1) it has good secondary working properties, (2) it has a high secondary recrystallization temperature and so has high high-temperature strength, and (3) it has stable electron release characteristics, and it is of very great industrial value.

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⑤④構造材用モリブデン

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⑫発 明 者 清宮元男
横浜市磯子区新杉田町8番地東京芝浦電気株式会社横浜金属工場内

⑫発 明 者 清水忠
横浜市磯子区新杉田町8番地東京芝浦電気株式会社横浜金属工場内

⑪出 願 人 株式会社東芝
川崎市幸区堀川町72番地

⑭代 理 人 弁理士 津国肇

明 細 書

1. 発明の名称

構造材用モリブデン

2. 特許請求の範囲

1. モリブデン（Mo）中に1～5重量%の酸化ランタン（La_2O_3）が均一に分散されており、該分散された酸化ランタン（La_2O_3）の個々の平均粒径が3 μm以下であつて、かつ、最大粒径が7 μm以下であることを特徴とする構造材用モリブデン。

2. モリブデン（Mo）粉末と酸化ランタン(La_2O_3)とからなる焼結体に加工率60%以上の加工を施して成る特許請求の範囲第1項記載の構造材用モリブデン。

3. 発明の詳細な説明

〔発明の技術分野〕

本発明は、La_2O_3粒子がMo中に均一に分散された構造材料用のモリブデンに関する。

〔発明の技術的背景とその問題点〕

La_2O_3を含有せるMo材は、主に電子管の陰極材として、コイル状（スパイラル状）の線または板を丸めた円筒として供される。

ところで、Mo中のLa_2O_3は酸化トリウム入りタングステン（ThO_2-W）中のThO_2と同様にMoと固溶したり化合物を形成することなく、Mo中にLa_2O_3の粒子として分散されている。

このため、このようなモリブデン材料の諸特性は、La_2O_3粒子の含有量のみならず、その分散状態の影響を大きく受ける。

例えば、Mo中のLa_2O_3が凝集している等、La_2O_3粒子の分散状態が悪い場合にはコイル状あるいは円筒状に賦形する等の二次加工を施す際に、しばしば断線したり、亀裂を生じるという問題が生じた。

また、上記の如くMo中のLa_2O_3の分散状態が悪いと、電子管の陰極材として用いた場合には良好な電子放出特性が得られにくく、しかも短寿命となるという種々の問題があつた。

しかしながら、従来、モリブデン材料に添加すべきLa_2O_3の適切な分散状態が知られていなかつ

たため、上記加工性、電子放射特性などの諸問題を解決することができなかった。

〔発明の目的〕

本発明の目的は、上記問題点を解消し、構造材として用いた場合には容易に二次加工ができ、しかも電子管の陰極材として用いた場合には長寿命となるLa_2O_3を1～5重量%含有するMo材を提供することにある。

〔発明の概要〕

本発明者らは上記目的を達成すべく、鋭意研究を重ねた結果、La_2O_3を1～5重量%含有するMo材において、Mo中にLa_2O_3粒子を均一かつ微細に分散せしめると、その二次加工性、電子放出特性等の諸特性が改善されることを見出し、本発明を完成した。

本発明の構造材用モリブデンは、モリブデン（Mo）中に1～5重量%の酸化ランタン（La_2O_3）が均一に分散されており、該分散された酸化ランタン（La_2O_3）の個々の平均粒径が3 μm以下であつて、かつ、最大粒径が7 μm以下であることを特徴とする。

本発明においてLa_2O_3は電子放出能を与え、かつ、高温強度を高める成分である。

La_2O_3の含有量は1～5重量%とする。La_2O_3の含有量が1%未満の場合はLa_2O_3の添加効果が得られにくく、純Moに近い特性を示し、5%を超えた場合は、5%以下の添加効果と、さほど大きな変化が認められず、しかも、二次加工性が悪くなる等の問題点を生じる。

La_2O_3の粒子径は平均粒径で3 μm以下であり、かつ、最大粒径で7 μm以下でなければならない。平均粒径が3 μmを超えるか、または最大粒径が7 μmを超えると、線または板を二次加工する際に断線したり、亀裂が入る等、著じるしく加工性が低下するばかりでなく、電子管の陰極材料として用いた場合、長時間安定な電子放出特性を得ることが困難となる。

更に、線あるいは板材の二次加工性は、La_2O_3の含有量、分散形態の他に、モリブデン（Mo）と酸化ランタン（La_2O_3）からなる焼結体からの加工率（横断面積の変化率）に影響される。

本発明の構造材用モリブデンは、好ましくは、焼結体からの加工率60%以上で加工されたものである。Moの様に、もともとCu，Alなどと比較して脆い金属は、焼結によつて生じる方向性のない結晶組織を、加工することによつて、その加工方向に配向した結晶組織を形成させることができる。このような集合組織を形成させることによつて構造材用モリブデンの柔軟性が向上する。La_2O_3 1～5重量%含有せるMo材において、発明者の実験結果によれば、焼結体からの加工率は、大きくなる程二次加工性が容易となるが、60%以上の加工率を有する線、あるいは板材であれば、実用上問題ない。

〔発明の実施例〕

以下本発明のLa_2O_3 1～5重量%含有せるMo材の特徴を説明する。

粉末冶金法によつてLa_2O_3含有量を0.5，1.0，2.0，4.0，6.0重量%、さらにLa_2O_3粒径に差が出る様、添加量、混合方法を変え、機械プレスにより1.5 ton/cm²の圧力で圧粉体を作り、この圧粉体を1850℃で8時間水素雰囲気中で焼結した。この時得られた焼結体は、比重が約9.50、断面が12×12 mm、長さ650 mmの形状であつた。この焼結体を温度を加えながら転打加工、引抜き加工を施し、0.60 mmφの線を得た。Mo線中のLa_2O_3粒子径の確認は、線を熱硬化性樹脂の中に埋込み、通常の研磨法により鏡面仕上後、特殊な電解研磨法によりMo材のみを研磨し、La_2O_3を研磨面に浮き上がらせる様に残留させた後、走査型電子顕微鏡により観察した。

線径0.60 mmφにおけるMo中のLa_2O_3含有量及び、La_2O_3の最大粒子径と線の柔軟性、二次再結晶温度との関連を第1表に示した。

第1表

La_2O_3 含有量(%)	0.5	1.0	2.0	4.0	6.1
La_2O_3 の最大粒子径(μm)	1.2	5.3	9.2	1.1	4.9	9.6	0.9	4.5	8.0	9.7	0.9	5.2	9.4	0.9	4.5
0.6㎜φ引抜き加工上り の折り曲げ回数 (相対比較)	1	8.0	1.3	10.1	8.0	0.9	9.6	8.0	0.9	10.4	9.0	7.9	0.5	1.8	0.1
1500℃×5分焼鈍後	1	8.0	1.2	4	3	0.7	4	4	0.3	0.5	4	3	0.6	[redacted]	0.1
0.6㎜φの二次再結晶温度 (℃)	1400	1400	1400	1700	1700	1700	1800	1800	1800	1800	1750	1750	1750	1750	1750

これから明らかな如く、La_2O_3 の含有量は1.0～5重量%が最も[redacted]本発明者らの実験結果によれば2～3重量%が最も適正な量である。又、La_2O_3 の粒子径は小さい方が良く、8 μm を超えると二次加工性は急激に低下する。

また、上記圧粉体を2 ton/㎠の静水圧でプレスし、圧粉体を成形し、水素雰囲気中にて1850℃×8時間焼結して得られた比重9.45、直径60㎜φ、長さ400㎜の形状の焼結体をハンマー加工、ロール加工し厚さ0.2㎜の板を得た。この時、中間で、水素雰囲気中にて二次再結晶温度以上で熱処理した。熱処理する板材の寸法は、板厚0.2㎜に加工する迄の加工率が40%，60%，80%とした。この時の板材の柔軟性について調査した結果を第2表に示す。

第2表

加工率(%)	40	60	80
0.2tの板材の折り曲げ性 (相対比較値)	1.5	10	20

※ La_2O_3 添加量2%
La_2O_3 の最大粒径は2.0 μm

この結果から明らかな如く60%以上加工を施工された板材の柔軟性が良いことがわかる加工率による柔軟性効果は、他の場合もまったく同様である。

次に電力管（線径0.2㎜φ）を用いMo中のLa_2O_3含有量と、電子放出特性との関連性を第3表に示す。第3表によると、La_2O_3 の含有量は1.0重量%以上必要であり、6.0重量%を超えても電子放出特性は良くならず、むしろ2重量%の特性に比較して若干、低下傾向がある。

第3表

La_2O_3 含有量(%)	0.5	1.0	2.0	6.0
初期の電子放出特性 (陰極加熱温度1600℃) (相対比較値)	1	15	25	14
寿命 (安定で連続した電子放出特性が得られなくなる時間の相対比較値)	1	13	18	13

〔本発明の効果〕

以上の説明から明らかな様に本発明の構造材用モリブデンは、

①その二次加工性が良好であること、②二次再結晶温度が高く、従つて高温強度が高いこと、③電子放出特性が安定で、かつ、優れること等の効果を奏し、その工業的価値は極めて大である。